CORNER BROOK PULP AND PAPER MILL WASTE MANAGEMENT

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FINAL REPORT

Corner Brook Pulp and Paper Mill Waste Management

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Executive Summary

The fly ash generated from Corner Brook Pulp and Paper Limited was transformed to activated carbon through physical activation process in a high temperature tube furnace in this study. Effects of two factors including activation temperature and activation time were investigated. Iodine number, methylene blue value, surface microstructure, surface area and pore volume were all analyzed to assess the adsorption capacity of different carbon samples. In this study, the sample activated under 850 °C for 2 hours has the highest iodine number (704.53 mg/g) and methylene blue value (193.47 mg/g). Hence, it is selected to conduct further assessment on surface area and pore volume. Comparing the CBPP FA-Clean sample with the CBPP FA-850 °C-2hr sample, it is investigated that the surface area was significantly increased from 486.44 m^2/g to 847.26 m^2/g. Meanwhile, the pore volume increased from 0.18 cm^3/g to 0.28 cm^3/g. The result of scanning electron microscopy also reveals that there are lots of pores developed on the sample surface after activation at 850 °C for 2 hrs.

Batch test was conducted to evaluate the adsorption efficiency of the CBPP FA-850 °C-2hr on natural organic matter removal. The isotherm revealed that the use of 0.5 g (AC) /L (water) has the highest adsorption effectiveness, it is hence selected as the dose in column filtration experiment. A column filtration technology was then developed to further evaluate the adsorption capacity of the activated carbon. The column is 30 cm length and 40 mm diameter, and the CBPP FA-850 °C-2hr sample was placed at the bottom of the column to act as a carbon barrier. Water sample from a local community was continuously passed through the column for 24 hours. The organic matter, measured as total organic matter, in the water sample before and after the filtration was analyzed. Results indicate that more than 60% of the organic matter can be removed by the carbon barrier within 2 hours filtration. It is also discovered that the carbon barrier is more effective in the adsorption of light-sensitive organic matters.

Above all, this study can not only help CBPP with their waste management, but also provide a cost-effective approach which can be potentially applied in the water treatment field.

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1 Background Information

1.1 Current waste management status in Corner Brook Pulp and Paper Ltd.

Corner Brook Pulp and Paper (CBPP) Ltd. utilizes a thermo-mechanical pulping process to produce standard newsprint and other specialty newsprint grades. The unit production capacity of CBPP has reached almost 700 tons of newsprint per day, and the plant plays an important role in promoting the economic growth of western Newfoundland.

The pulp and paper manufacturing process is supported by steam generated from mill boilers. The main boiler (#7) in CBPP burns a mixture of Bunker C fuel, waste oil fuel, and hog fuel, while the backup or supplementary boilers (#3 and #6) combust Bunker C fuel. Bunker C fuel, also known as No. 6 Fuel oil, is a high-viscosity residual oil. Hog fuel is a mix of coarse chips of bark from trees, saw dust, and wood fiber. To control air emissions released to the atmospheres during the mill operation, the main boiler is equipped with emission control devices including mechanical dust collectors, low oxides of nitrogen (NO_x) burners, and a wet scrubber. Each year, a significant amount of fly ashes, including boiler ash and bottom ash, are generated from mill operation and disposed to landfills (Department of Environment and Climate Change, 2017).

1.2 Application of activated carbon derived from fly ash

The application of activated carbon derived from fly ash can be utilized in both gas and water treatment for the adsorption of various contaminants, and related studies have been done by many researchers. Aslam et al. (2015) have synthesized activated carbon from oil fly ash. The removal of H_2S from industrial gas stream by the activated carbon was analyzed, and a maximum of 0.3001 mg/g adsorption capacity has been reached. Salehin et al. (2016) studied the removal of different heavy metals from aqueous solutions by the activated carbon generated from physical activation, and complete removal of copper and lead was observed at a neutral pH level. The adsorption of selenium in surface and groundwater using copper-impregnated activated carbon was investigated by Jegadeesan et al. (2015), the electrostatic forces are confirmed to have significant impact on the adsorption results. The activated carbon obtained from oil-fired fly ash has also been identified to be suitable for SO_2 and NO_x treatment in Davini's study (2002).

1.3 Previous work on fly ash

Our group has been working on the fly ash and extracted carbon and their potential application for many years. It is proved that the oil fly ash can be employed as a stabilizer or filling material in cement manufacture (Mofarrah, 2014). It can also act as an adsorbent which can effectively remove phenols, methylene blue, lead, and chromium VI from wastewater streams by up to 92% (Mofarrah and Husain, 2013; Mofarrah, 2014). Moreover, the oil fly ash-derived activated carbon is capable of removing natural organic matter from intake water sources for the local communities (i.e., Pouch Cove, Torbay, etc.) in NL. Results of the case study in Pouch Cove indicates that more than 70% of the organic matter has been removed from the source water, it thus prevented the formation of disinfection by products in their drinking-water supply system (Husain et al., 2012; Ahmad, 2013).

1.4 Objective and scope of work

The objective of the study is to convert the waste materials (i.e. fly ash) into a valuable product which can then be utilized to improve water quality in source water pretreatment in local communities. The finding of the study will reduce the amount of ashes ending up in landfill and thus save the landfill space and associated disposal cost.

Although commercial available activated carbon has proven applications in filtration technology for water and wastewater treatment for the removal of various contaminants, it is not widely employed at many industrial plants due to the high cost of raw precursor materials. Therefore, there is a trend to find alternative cost-effective precursors from wastes and industrial by-products (Ahmed and Dhedan, 2012; Gode and Pehlivan, 2006). The conversion of waste products into adsorbents for pollution control would not only help in reducing the disposal cost but also provide a cost-effective alternative for the activated carbon generation (Kurniawan et al., 2006).

Among industrial wastes, carbon-rich fly ash has been extensively studied for the adsorptions of both inorganic and organic pollutants from air and aqueous solutions (Banerjee et al., 2004; Sarkar and Acharya, 2006). One major reason for selecting ashes from pulp and paper mill for activated carbon development is that the mill boilers generally combust residual oil and wood residue which leads to high carbon content in fly ash. Preliminary analysis of the CBPP fly ash indicates that its carbon content is around 80%, which is quite high and suitable to be utilized as an adsorbent in developing a cost-effective filtration technology.

In this study, raw fly ash from CPBB will be firstly characterized and cleaned to eliminate the impurities. The cleaned carbon will then be activated at different activation temperatures for different activation times. The adsorption of iodine and methylene blue will be analyzed for the evaluation of surface area and pore volume development. The activated carbon with biggest surface area and pore volume will be applied in a column filtration technology. To determine the effectiveness of the developed activated carbon filtration technology, the intake source water from a local community was examined for the removal of organic matter through a 24-hour laboratory filtration experiment. The findings of this study will not only help CBPP Ltd. to save the cost of landfill and waste management, but also benefit the local communities in NL to improve their water quality.

2 Characterization of CBPP fly ash

Fly ash (FA) samples generated by CBPP were collected and delivered to the Environment Laboratory located in the Department of Engineering and Applied Science at Memorial University of Newfoundland.

2.1 Methodology

The raw FA sample was firstly grinded into powder before characterization. The raw powder sample was then washed with 5% HNO_3 solution on a carbon to acid ratio of 1 g per 10 mL at 60 °C for 2 hrs to recover unburnt carbon and remove impurities from the FA. After filtration, the particles were cleaned with distilled water for several times to eliminate any acid residue. At last, the filtered clean FA was dried at 110 °C overnight before activation use. Characterization of particle size, pH, moisture, ash content, carbon content, Iodine number, methylene blue value, and metal elements were conducted for both raw and clean FA samples. Detailed methods are listed in the following sections.

2.1.1 Particle size

The particle size of raw FA sample after grinding was determined by using a Horiba Particle Laser Scattered Particles Size Analyzer (Model LA-950) in Earth Resources Research and Analysis Facility (TERRA).

2.1.2 pH

The pH of the samples was analyzed following the ASTM method D38738-05 (2017). Simply, 100 mL of boiling deionized water was added to 10 g of an FA sample and kept boiling on the hot plate for 15 mins. The filtrate was then cooled to room temperature, and a pH meter was used to measure the pH values of raw and clean FA samples.

2.1.3 Moisture content

Moisture content was determined by the ASTM method D2867-09 (2014). A crucible with lid was weighed and recorded. A 2 g FA sample was weighed and transferred into the crucible, and the crucible and lid were dried in a conventional oven at 110 ± 5 °C to a constant weight. After cooled down to room temperature in a desiccator, the crucible and lid were weighed again. The moisture content can be calculated as

$$M\% = \frac{w_{wet} - w_{dry}}{w_{sample}} \times 100$$

in which,

$M\%$ = moisture content in w/w%,

w_{wet} = weight of crucible with lid plus original raw sample, g,

w_{dry} = weight of crucible with lid plus dried sample, g,

w_{sample} = weight of original raw sample, g.

2.1.4 Ash content

ASTM method D2866-11 (2011) was followed in this section to evaluate the ash content in the FA samples. A crucible was burned in a muffle furnace at 650 °C for 1 hr, cooled to room temperature in a desiccator. The weight of crucible was then recorded. The FA sample was dried at 110 ± 5 °C in a conventional oven to remove the moisture. A certain amount of the dried sample was weighed and transferred to the crucible and the crucible was placed in a muffle furnace at 650 °C for 3 to 16 hrs to achieve constant weight. The ash content can be calculated as

$$Ash\% = \frac{w_{ash}}{w_{sample}} \times 100$$

in which,

$Ash\%$ = ash content in w/w%,

w_{ash} = weight of ash, g,

w_{sample} = weight of original sample, g.

2.1.5 Carbon content

The carbon content of the samples before and after the cleaning process were examined by a Perkin – Elmer 2400 Seriers II CHN analyzer in Aquatic Research Cluster (ARC) under Core Research Equipment & Instrument Training (CREAIT) Network.

2.1.6 Metal content

The major and trace metals were analyzed for raw and clean FA samples by a Perkin – Elmer ELAN DRC II Mass Spectrometer in TERRA facilities under CREAIT Network.

2.1.7 Iodine number

The iodine number (IN) is defined as the amount of iodine adsorbed by 1 g of carbon tested. It has been proved to have sort of correlation to micropore volume and surface area (Krupa and Cannon, 1996; Rufford et. al, 2014), thus is commonly used to measure the micropore content in

a carbon sample. In this case, it was determined by following the ASTM method D4607-14 (2014). About 0.2 gram of the carbon sample was mixed with 15 mL 0.1 N (normality) iodine solution in a 50 mL Erlenmeyer flask. The flask was then placed on a laboratory shaker and shaken for 15 mins at 200 rpm. When the shaking was finished, the carbon sample was filtered out and 10 mL of the filtrate was titrated with 0.1 N sodium thiosulfate solution. A few drops of starch solution was used as the indicator for titration. The iodine number can be calculated as

$$IN = \frac{[(C_0 \times V_0) - (C_1 \times V_1 \times DF)] \times 126.90}{M_C}$$

in which,

IN = iodine number, mg/g,

C_0 = concentration of iodine solution, 0.1N,

V_0 = volume of iodine solution mixed with sample, mL,

C_1 = concentration of sodium thiosulfate solution, 0.1N,

V_1 = volume of sodium thiosulfate solution consumed in titration, mL,

DF = dilution factor, in this case is 1.5,

M_C = weight of carbon sample, g.

2.1.8 Methylene blue value

Methylene blue is one of the organic dyes that has been frequently used to characterize the mesoporous structures of a carbon sample since the molecular sizes of methylene blue are usually over 1 nm (Yan et. al, 2009; Attia et. al, 2008; Janoš et. al, 2003). The methylene blue value (MBV) is defined as the amount of methylene blue adsorbed by 1 g of carbon tested. The method applied to determine the methylene blue value is derived from GB/T 7702.6 (2008). In general, about 0.1 g of carbon sample was mixed with 10 mL methylene blue stock solution (1500 mg/L) in a 50 mL Erlenmeyer flask. The flask was then placed on a laboratory shaker and shaken for 30 mins at 200 rpm. After filtration, the filtrate was transferred to a 10 mm cuvette and analyzed for UV absorbance at the wavelength of 665 nm by using a UV/Vis spectrophotometer (Thermo Scientific Genesys). The methylene blue value can be calculated as

$$MBV = \frac{(C_0 - C_1) \times V}{M_C}$$

in which,

MBV = methylene blue value, mg/g,

C_0 = concentration of methylene blue stock solution, mg/mL,

C_1 = concentration of methylene blue solution after filtration, mg/mL,

V = volume of methylene blue solution mixed with carbon, mL,

M_C = weight of carbon sample, g.

2.2 Results and discussion

2.2.1 Particle size

The particle size of raw FA sample was analyzed. Figure 2-1 shows the particle size distribution of the tested sample. From Figure 2-1, more than 25% of CBPP raw FA has the particle size of 15 to 31 μm; about 60% of it was evenly distributed in the range of 37 to 300 μm; the minimum and maximum particle sizes were 7.8 and 710 μm, respectively.

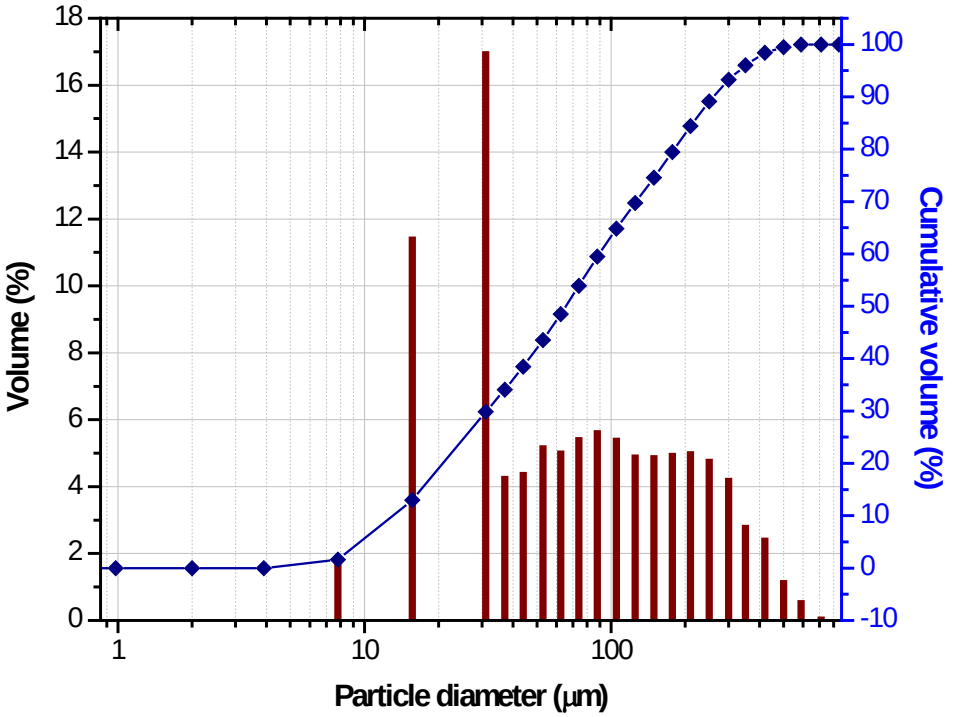

Figure 2-1 CBPP FA particle size distribution after grinding

2.2.2 pH, moisture content, ash content, carbon content, IN and MBV

The characteristics of pH, moisture content, ash content, carbon content, iodine number and methylene blue value for both raw and cleaned CBPP FA samples were examined. Results are shown in Table 2-1. Since the raw FA sample was cleaned by 5% HNO_3 solution, the clean FA shows strong acidity while the raw FA is alkaline. The acids left in the FA samples could be removed in the following activation process. Most moisture and ash content were reduced after the cleaning process, which indicates the effectiveness of using nitric acid solution as cleaning reagent. Meanwhile, the reduction of ash content also resulted in the increase of carbon content of the FA sample, which would further benefit the activation process. The iodine number decreased and the methylene blue value increased after cleaning, which means some impurities

in the raw sample reacted with the iodine other than the methylene blue. Accordingly, it is very necessary to conduct the cleaning process before any further treatment so that the evaluation of the carbon adsorption capacity will be accurate.

Table 2-1 Characterization of CBPP raw and clean FA samples

Parameters	pH	Moisture %	Ash content %	Carbon content %	IN (mg/g)	MBV (mg/g)
CBPP FA-Raw	11.44	1.67	14.04	78.68	444.56	57.42
CBPP FA-Clean	2.95	0.35	4.05	82.79	289.53	61.89

2.2.3 Metal content

The metal elements in CBPP FA were analyzed before and after the cleaning process, and results are shown in Table 2-2. The CBPP raw FA is rich in calcium, aluminum, iron and magnesium. After cleaned by 5% HNO_3 solution, about 44% of calcium was removed. Also, more than 60% of aluminum, and more than 70% of iron and magnesium were removed from the FA. It illustrates that the 5% HNO_3 solution is efficient in metal removal during the cleaning process.

Table 2-2 Metal contents in CBPP FA before and after acid-washing

Metal elements	Raw FA (Unit: ppm)	FA after washing (Unit: ppm)	Removal rate (%)
Magnesium (Mg)	511.65	185.33	63.8
Aluminum (Al)	947.025	281.31	70.3
Iron (Fe)	784.202	175.19	77.7
Zinc (Zn)	11.724	9.07	22.6
Copper (Cu)	7.280	1.75	76.0
Lead (Pb)	2.252	0	100
Arsenic (As)	<LD		
Vanadium (V)	15.460	2.57	83.4
Nickel (Ni)	15.962	3.74	76.6
Calcium (Ca)	2656.356	1481.50	44.2

3 Activation of CBPP Fly Ash

This study only focuses on physical activation of this wood based fly ash. Comparing with chemical activation, physical activation usually generates cleaner activated carbon (AC) products which are more suitable for water treatment technology development. Iodine number, methylene blue value, Scanning electron microscopy (SEM), as well as Brunauer, Emmett and Teller (BET) analysis were all used to assess the surface area and pore volume development. Since there are some limitations and difficulties in sending samples to other universities for analysis like BET, meanwhile, the analysis of iodine and methylene blue adsorption is more convenient to be done in our own lab, the iodine number and methylene blue value were mainly used as indicators for surface area and pore volume development. Only the sample with highest iodine number and methylene blue value was sent together with clean carbon sample for BET analysis.

3.1 Methodology

3.1.1 Effect of activation temperature

In this part, a programmable Lindberg/Blue M tube furnace was used for both carbonization and activation processes. The temperatures examined were 650 °C, 700 °C, 750 °C, 800 °C, 850 °C and 900 °C, respectively. In carbonization process, about 6 grams of the CBPP clean FA was firstly heated from room temperature to a desired temperature at a rate of 10 °C/min under N_2 flow (75 cm^3/min). Once reaching the desired temperature, the carbonization was continued for another hour. This was then followed by a 1-hour activation process under CO_2 flow (75 cm^3/min) at the same temperature. The AC samples generated at different temperatures together with CBPP raw and clean FA samples were analyzed for loss of ignition, iodine number, and methylene blue value. The sample with high iodine number and methylene blue value was selected to evaluate the effect of activation time.

3.1.2 Effect of activation time

In this part of experiment, the CBPP clean FA sample was carbonized and activated under the selected activation temperature for 1 hour, 2 hours, and 3 hours, respectively. The AC samples generated in this part were analyzed for iodine number and methylene blue value. The one with high iodine number and methylene blue value was employed in the following water filtration experiments.

3.1.3 Scanning electron microscopy (SEM)

To further evaluate the activation process, an SEM instrument from TERRA facilities was used to observe the surface microstructure and morphology of the carbon sample before and after activation.

3.1.4 Surface area and pore volume

The clean and activated samples were sent to the Centre for Catalysis Research and Innovation (CCRI) in the University of Ottawa for surface area and porosity analysis. The surface area and pore volume were measured by N_2 gas adsorption at 77 K using a 3Flex Surface Characterization Analyzer (Micromeritics Instrument Corporation). Fundamental principle was shown in another Harris Centre final report (Ling et al., 2016). In general, the surface area (m^2/g) was measured from the adsorption isotherm by the Brunauer, Emmett and Teller (BET) equation (Equations 3-1 to 3-5), using the relative pressure range of 0.05-0.35, considering that the area of the N_2 molecule is 0.162 nm^2 at 77K (Rodriguez-Reinoso, 1997). The total pore volume, V_T, was obtained from the N_2 adsorption isotherm at $p/p_0 = 0.99$.

$$\frac{1}{v\left(\frac{P_o}{P}-1\right)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{p_o}\right) \tag{3-1}$$

$$v_m = \frac{1}{S+I} \tag{3-2}$$

$$c = 1 + \frac{S}{I} \tag{3-3}$$

$$SA_{BET} = \frac{(v_m N A_{(N)})}{v} \tag{3-4}$$

$$S_{BET} = \frac{SA_{BET}}{a} \tag{3-5}$$

in which,

v = volume of adsorbed N_2 gas at standard temperature and pressure (STP);

P & P_0 = the equilibrium and saturation pressures of the adsorbate;

v_m = volume of gas (STP) required to form one monolayer;

c = BET constant related to energy of adsorption;

N = Avogadro's number (6.02E+23);

$A_{(N)}$ = cross section of N_2 (0.162 nm^2);

SA_{BET} = total BET surface area (m^2);

S_{BET} = specific BET surface area (m^2/g);

a = mass of adsorbent (in g).

The BET surface was calculated from the BET equation by plotting $1 / v [(P_0 / P) - 1]$ on the y-axis and P/P_0 on the x-axis in the range of $0.05 < P/P_0 < 0.35$. The slope (S) and the y-intercept (I) of the plot were used to calculate v_m and the BET constant c.

3.2 Results and discussion

3.2.1 Effect of activation temperature

The CBPP activated carbon samples were evaluated by determining the loss of ignition, iodine number and methylene blue value. Results are shown in Table 3-1. Iodine number and methylene blue value are also shown in Figure 3-1. From Table 3-1, the loss of ignition basically increases when the activation temperature increases. The loss in the activation process is mainly due to the reaction between C and CO_2 (Chang et. al, 2000). When the activation temperature increases, the reaction will be accelerated, which will therefore result in a higher loss.

Iodine number and methylene blue value are two parameters that are commonly used to assess the performance of activated carbon. Iodine adsorption implies the micropore content of an AC sample, while the adsorption of methylene blue can give a hint about the mesopore structure (Itodo et. al, 2010). From Figure 3-1, it is clearly that both iodine number and methylene blue value increase when the activation temperature increases. It illustrates that higher temperature results in higher level of micropore and mesopore development. However, the higher activation temperature applied, the higher ignition loss obtained. For the sample activated under 900 °C, it has the most micropores and mesopores while the loss of ignition could be higher than fifty percent. It is not cost-effective to generate activated carbon with high energy consumption and loss of ignition. Comparing with activated carbon generated under 900 °C, the one obtained at 850 °C shows relative high level of micropore and mesopore, and relative low level of ignition loss. The 850 °C is then selected to evaluate the effect of activation time.

Table 3-1 Characterization of CBPP FA and AC samples

Samples	Loss of ignition (%)	Iodine No. (mg/g)	Methylene blue value (mg/g)
CBPP AC-650°C	7.79	529.66	71.57
CBPP AC-700°C	14.29	552.92	73.84
CBPP AC-750°C	13.70	469.26	76.7
CBPP AC-800°C	22.22	502	107.19
CBPP AC-850°C	36.84	515.16	142.98
CBPP AC-900°C	53.75	760.91	169.33

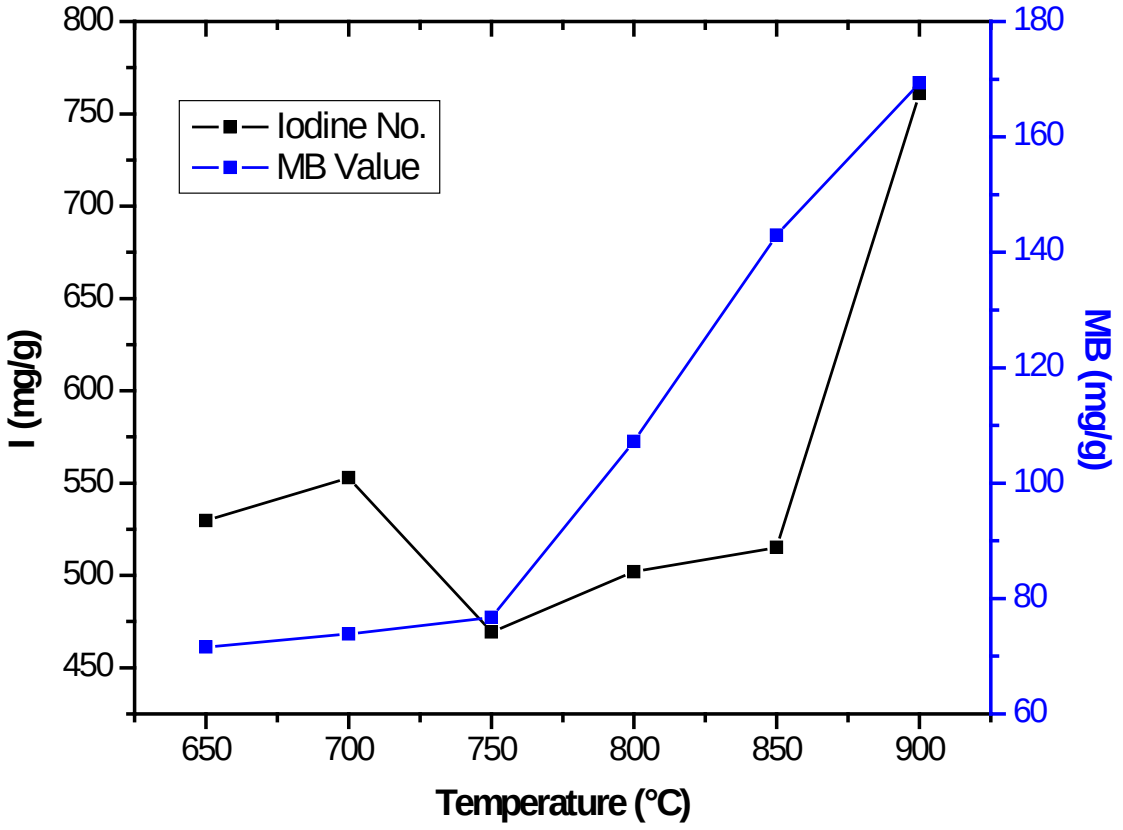

Figure 3-1 Iodine No. and MB value of CBPP samples activated at different temperatures

3.2.2 Effect of activation time

After testing different activation temperatures, different activation time periods were also examined. Results of iodine number and methylene blue value were shown in Table 3-2 and Figure 3-2. The results of iodine number and methylene blue value illustrate that the sample being activated under 850 °C for 2 hours has the most micropores and mesopores. It is hence selected to conduct the adsorption tests on real water samples.

Table 3-2 Characterization of 850°C-activated CBPP AC samples

Samples	Iodine No. (mg/g)	Methylene blue value (mg/g)
CBPP AC-850°C-1hr	515.16	142.98
CBPP AC-850°C-2hr	704.53	193.47
CBPP AC-850°C-3hr	617.63	148.24

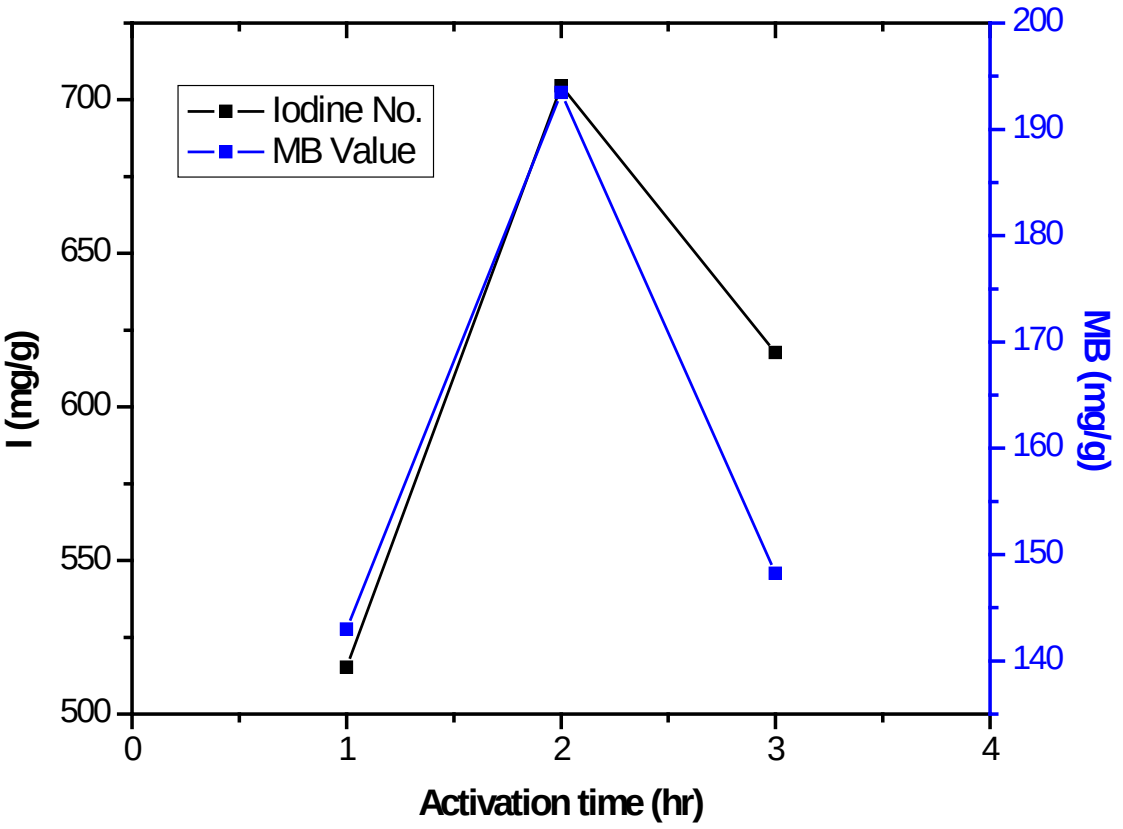

Figure 3-2 Iodine No. and MB value of CBPP samples activated with different time lengths

3.2.3 Scanning electron microscopy (SEM)

The surface microstructure images of CBPP FA-Clean and CBPP AC-850°C-2hr are observed by SEM and shown below. Comparing Figure 3-3 (a) with (b), a dense porous structure was formed after activation, which is in accordance with the results of iodine and methylene blue tests.

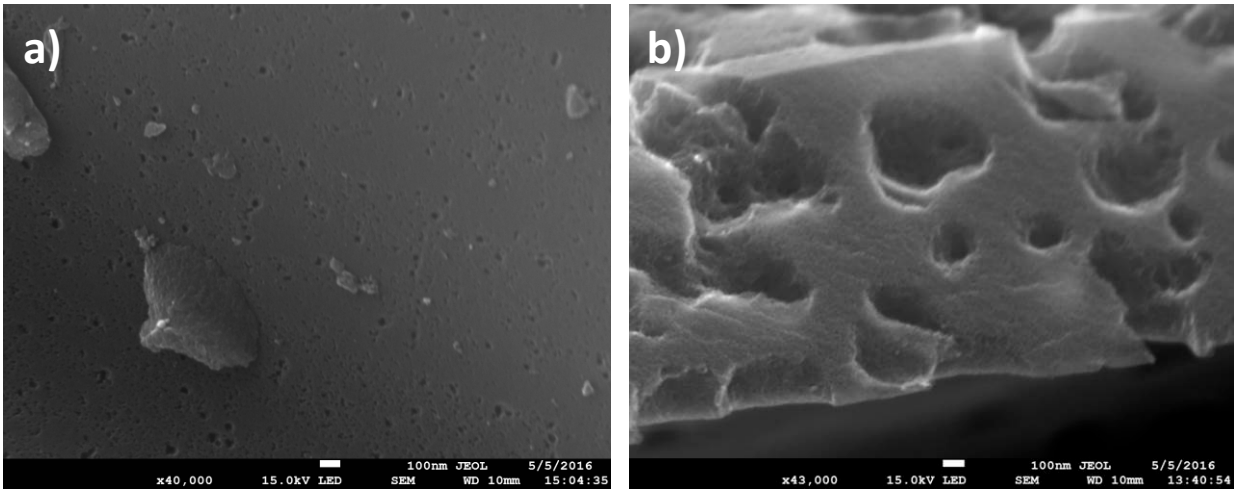

Figure 3-3 SEM images of carbon particles surface microstructures: (a) before activation; (b) after activation

3.2.4 Surface area and pore volume

The BET surface area and porosity analysis was conducted to further assess how well the CBPP carbon has been activated. As listed in Table 3-3, there is a significant improvement on surface area, micropore area and pore volume in the sample after activation. Nitrogen (N_2) adsorption-desorption isotherm curves for both samples are also plotted in Figure 3-4 and Figure 3-5, respectively. It is revealed that the adsorption rate of the carbon sample is highly improved after activation, which is also in accordance with the iodine and methylene blue test results. More information of BET surface area and porosity analysis can be found in appendices A and B.

Table 3-3 Surface area and pore volume of CBPP clean and activated carbon

Samples	Surface area (m^2/g)	Micropore area (m^2/g)	Pore volume (cm^3/g)
CBPP FA-Clean	486.44	402.50	0.18
CBPP AC-850°C-2hr	847.26	619.49	0.28

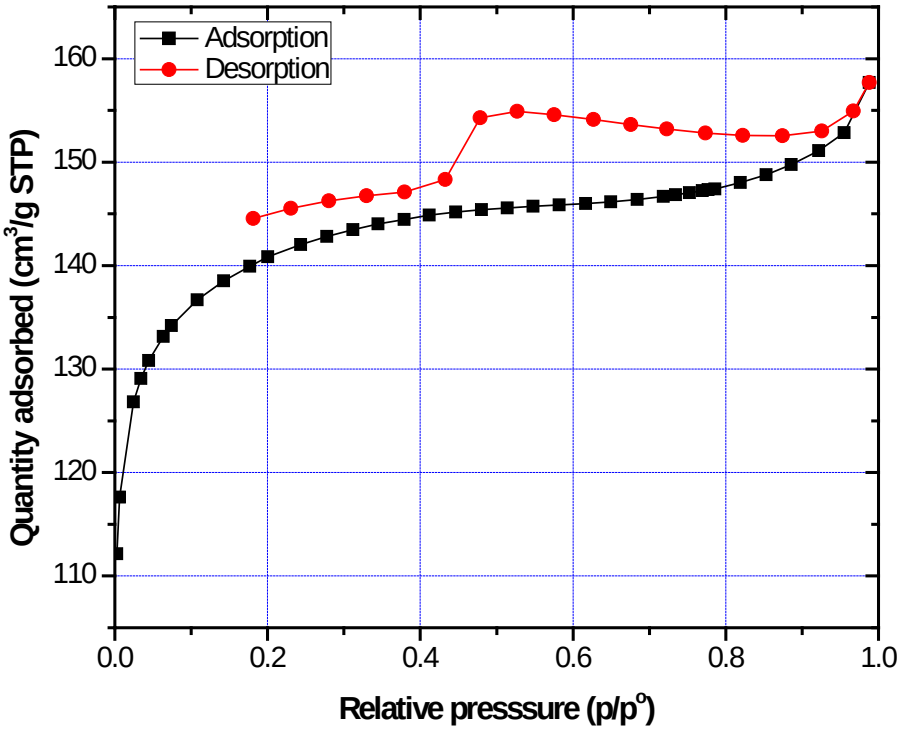

Figure 3-4 N_2 adsorption-desorption isotherm linear plot of CBPP FA-Clean

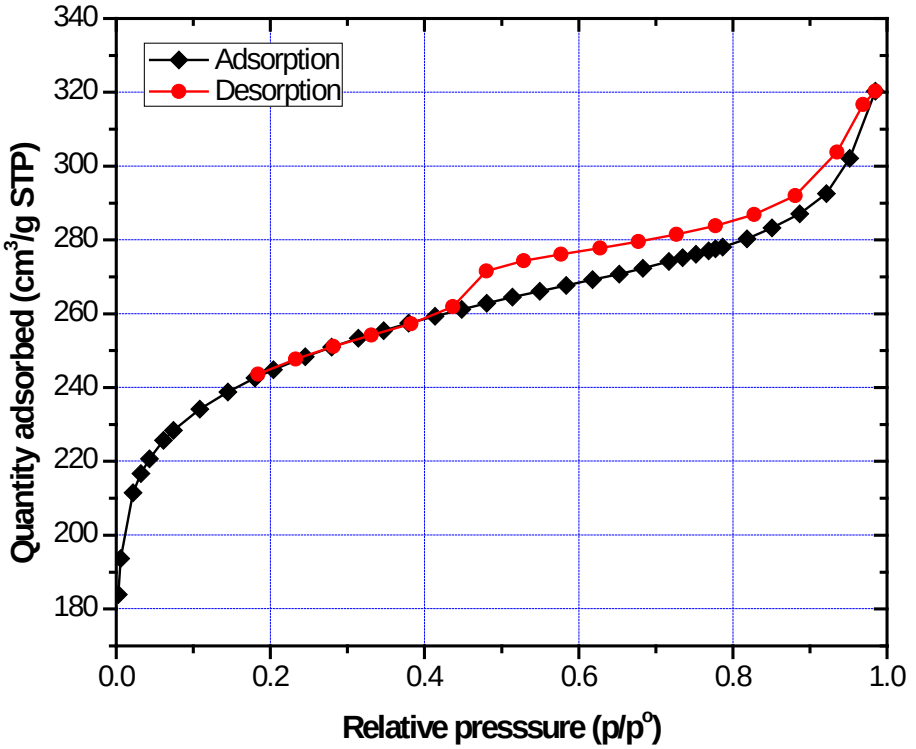

Figure 3-5 N_2 adsorption-desorption isotherm linear plot of CBPP AC-850°C-2hr

4 Batch Test Evaluation of CBPP Activated Carbon

After evaluating the adsorption capacity of iodine and methylene blue by CBPP AC, real water samples was applied to further evaluate the adsorption of organic matter through batch test. Small rural communities in NL are suffering from the problem of disinfection by products (DBPs) in their drinking water for many years. Since those communities have very small populations and are lack of sufficient budget to install and maintain water treatment facilities, the most common way of source water pretreatment is to add chlorine for disinfection purpose (ENVC, 2015). Once the source water contains high level of natural organic matters, the DBPs, which have been identified as potential health hazards in long-term exposure, are formed in the drinking water (USEPA, 2009; ENVC, 2009a). Hence, this part of study mainly evaluated the performance of the CBPP AC-850°C-2hr on the adsorption of natural organic matters in real water samples using a jar test.

4.1 Characterization of water samples

4.1.1 Methodology

The source water sample was collected from a local community that highly concerns about the DBPs in their drinking water systems. The natural organic matter in the source water was characterized by measuring the total organic carbon (TOC). Other parameters of pH, alkalinity, color, turbidity, UV at the wavelength of 254 nm, and total dissolved solids (TDS) were also characterized.

4.1.2 Results and discussion

The characteristics of the source water sample are listed in Table 4-1. The pH, turbidity and TDS of the analyzed source water are all within the Canadian drinking water quality guidelines. Only the level of color exceeds that in the guideline. Color is prevalent in natural source waters especially surface waters. The higher level of color indicates more organic matter in the water.

Table 4-1 Characteristics of community intake source water

Parameters	Alkalinity* (mg/L)	Color* (TCU)	pH	Turbidity (NYU)	UV_{254} (A)	TDS* (mg/L)	TOC (mg/L)
Canadian drinking water quality guidelines	NA	15	6.5 ~ 8.5	1.0	NA	500	NA
Source water	7.00	31	6.67	0.24	0.271	21	8.472

(* Source: Newfoundland and Labrador Water Resources Portal)

4.2 Evaluation of organic matter adsorption through jar test experiments

4.2.1 Methodology

Jar tests were conducted to evaluate the adsorption of organic matter by different CBPP AC dose and for different contact times. In this experiment, different amount of the CBPP AC-850°C-2hr sample was mixed with a series of 500 mL source water at ratios of 0.5 g/L, 1 g/L and 2 g/L. The mixtures were thoroughly mixed on magnetic stirrers for adsorption time of 15 mins, 30 mins and 60 mins, respectively. The mixtures were filtered by 0.45 μm membrane filters and the filtrates were analyzed for TOC and UV. Since natural organic matter is commonly measured as TOC, it is used to quantify the natural organic matter in the water samples. It is believed that some natural organic matter compounds have certain chemical structures that can absorb UV light especially at the wavelength of 254 nm (ENVC, 2009b). Hence, UV_{254} is also applied in the quantification of the natural organic matters. Besides AC dose and contact time, temperature and pH can have influences on the adsorption of organic matter as well. However, the adsorption tests in real cases were usually conducted at room temperature, and the pH of the source water does not have much fluctuation in different seasons. The effects of temperature and pH are therefore not considered in this study.

4.2.2 Results and discussions

The adsorption capacity of CBPP AC was examined through batch tests. TOC removal and UV deduction were investigated and shown in Figure 4-1 and Figure 4-3. As can be seen in Figure 4-1, 75% of TOC was removed after 60 mins adsorption at a dose of 0.5 g/L. The trend of TOC removal at dose of 1 g/L is similar to that at 2 g/L from 15 mins to 60 mins. About 85% of TOC removal was found from 30 mins to 60 mins at both doses, which indicates that the maximum adsorption of TOC is around 85% and it can occur within 30 mins of adsorption. As shown in Figure 4-3, a 72% of UV_{254} deduction was observed after 15 mins adsorption at the dose of 0.5 g/L, meanwhile a 95% of UV_{254} deduction was obtained after 60 mins at the same dose. For the doses of 1 g/L and 2 g/L, the UV_{254} was dramatically decreased to zero within 15 mins of

adsorption, which illustrates the CBPP AC is extremely effective in UV_{254} deduction in the adsorption experiments. Comparing TOC removal with UV_{254} deduction at the carbon dose of 1 g/L with 15 mins adsorption time, 74% of TOC was removed while 100% UV_{254} deduction was detected. As stated earlier, both TOC and UV were used to quantify the organic matter. The big difference in the TOC removal and UV deduction results implied that some of the organic compounds in the water sample cannot absorb UV light at the wavelength of 254 nm. From another point of view, it also illustrates that this CBPP AC is more effective in the adsorption of light-sensitive organic matters. The same phenomenon was also discovered in the column experiment in the next chapter.

Figure 4-2 displays the TOC adsorption isotherm by CBPP AC with different doses. From the isotherm, the adsorbed TOC by each gram of activated carbon is 3.7 mg/g, 1.1 mg/g and 0.6 mg/g for doses of 0.5 g/L, 1 g/L and 2 g/L, respectively. The use of 0.5 g (AC) /L (water) in the batch test has the highest adsorption effectiveness and the lowest cost of AC. This dose is thus determined to be appropriate in the following experiment.

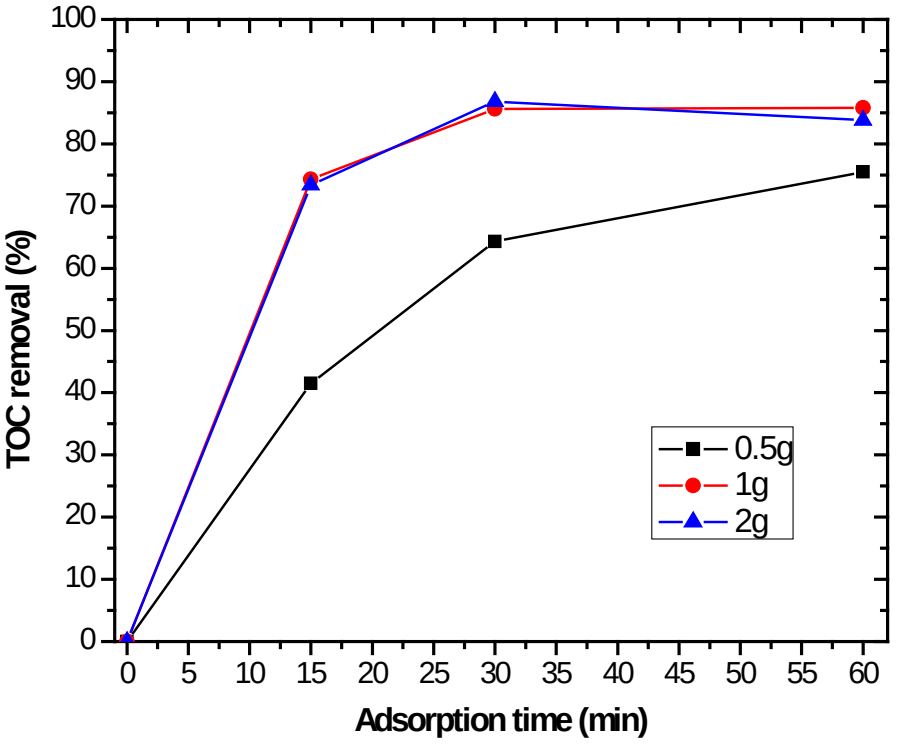

Figure 4-1 TOC adsorption kinetics by CBPP AC with different doses

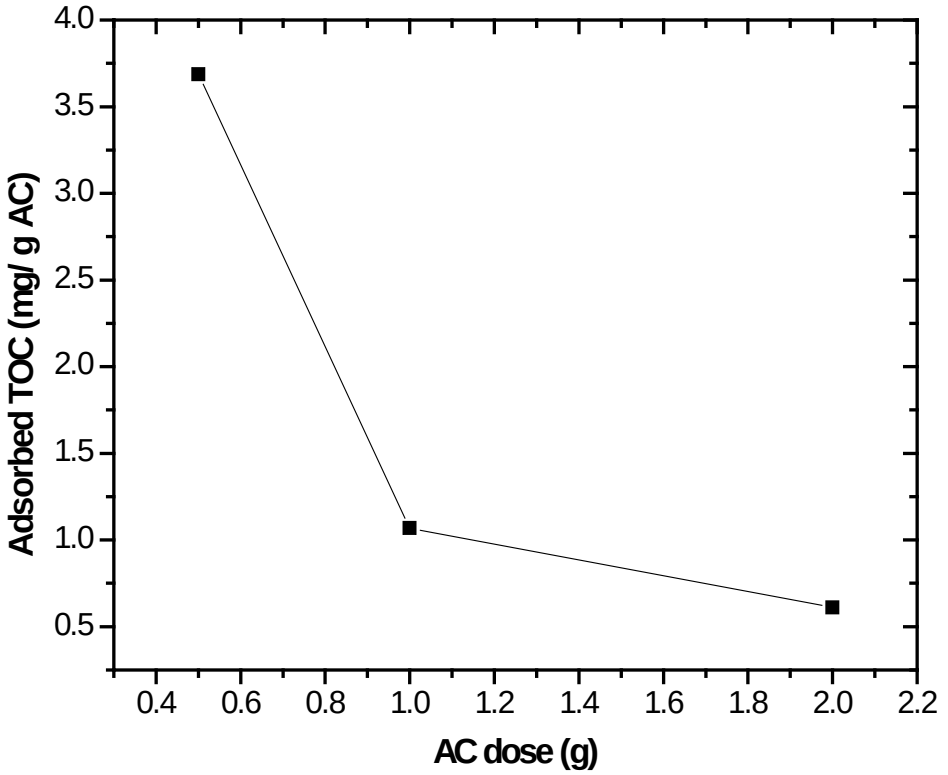

Figure 4-2 TOC adsorption isotherm by CBPP AC with different doses

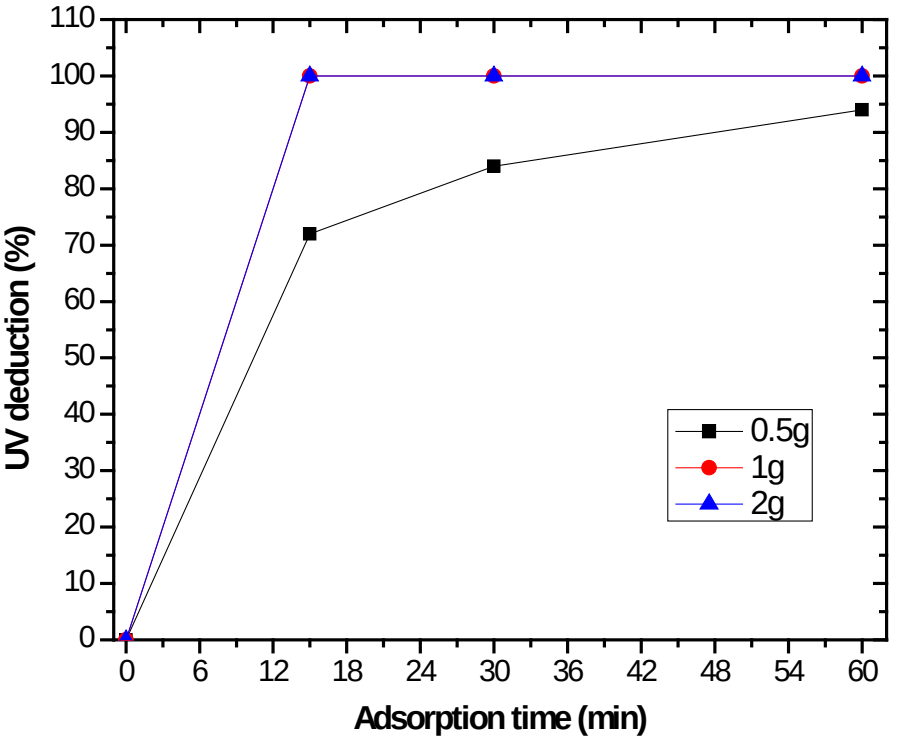

Figure 4-3 UV deduction by CBPP AC with different doses

5 Development of Carbon Filtration Technology

Carbon filtration technology has been widely applied in water and wastewater treatment for many years. Commercialized carbon filtration systems are frequently designed to be in the form of fixed bed adsorption units. Hence, in the last part of this study, a lab scale fixed bed carbon filtration system was developed, and a preliminary test was conducted to estimate the adsorption efficiency of CBPP AC on natural organic matter in real water samples.

5.1 Design of a carbon filtration system

An acrylic glass column with 30 cm length and 40 mm diameter is made to implement the carbon filtration technology in the lab. In general, a 0.45 µm membrane filter paper is placed at the bottom of the column and 5 g CBPP AC-850°C-2hr sample is then packed into the column. The column top part is connected to a water reservoir which contains water samples to be treated, and the water will pass through the column in a down flow mode. A peristaltic pump is connected at the column outflow to control the filtration speed. A sketch of the filtration system is displayed in Figure 4-1. When the water enters the column, and passes through the carbon barrier, the natural organic matter in water can be adsorbed by the activated carbon so that the formation of DBPs can be avoided or mitigated.

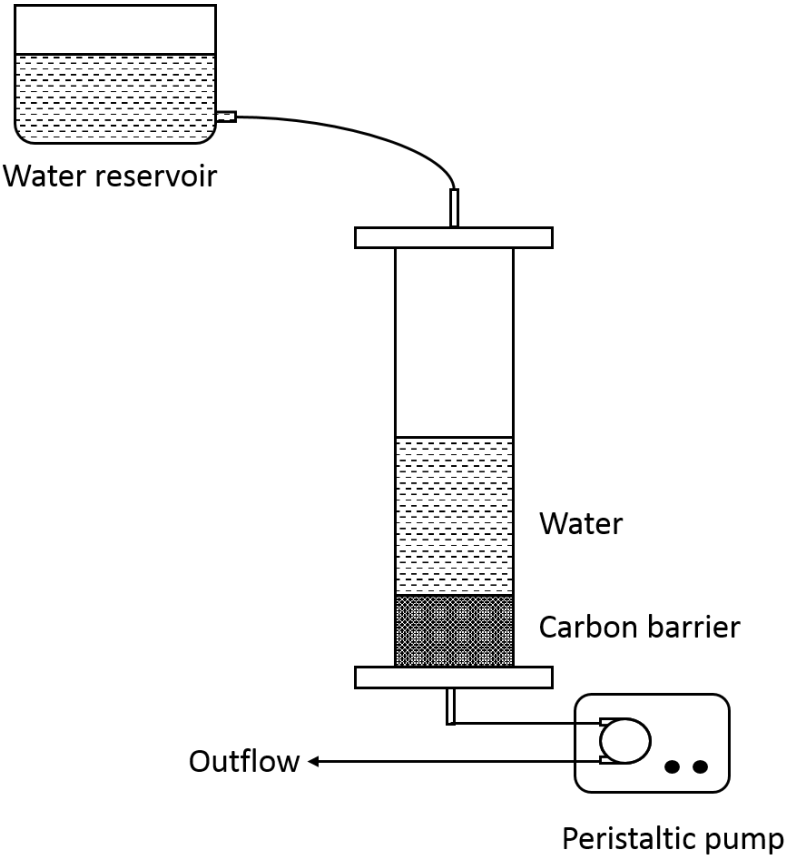

Figure 5-1 A sketch of carbon filtration system

5.2 Evaluation of system performance

5.2.1 Methodology

A 24-hr column filtration test was conducted to evaluate the adsorption performance of the AC sample. The source water passed through the column in a down flow mode. The flow rate of this test was kept in the range of 6 to 8 mL/min and about 10 L in total of the source water has been filtered within the 24-hr period. In this study, the filtrate samples collected at the column outlet at the 1st, 2nd, 3rd, 6th, 12th and 24th hr were analyzed for both TOC and UV_{254}.

5.2.2 Results and discussion

5.2.2.1 TOC

From Figure 4-2, the TOC of the column effluent samples decreases from 8.472 mg/L to 3.2 mg/L in the first two hours, and then increases to 7.8 mg/L at the twenty-forth hour. The TOC in column effluent could have such a trend is mainly due to the unstable flow rate. Since the CBPP AC used in column test is in powder form, it can cause blocking problems sometime in the middle of the experiment. The flow rate is usually high in the beginning of the filtration, and it

will gradually become slow. When the flow rate slows down, the contact time between carbon and water sample will be extended. Therefore, the TOC in the column effluent was decreasing in the first few hours. To overcome the blocking problem, a granular type of activated carbon is suggested in future study.

Comparing the original source water with the column effluent sample at the end of the second hour, more than 60% of the organic matter has been adsorbed or removed by the carbon barrier. After 2 hours, the organic matter in the column effluent starts to increase but still below the original level, which implies that the adsorption rate of the carbon barrier is decreasing. After 24 hours, the TOC of the column effluent sample is close to 8 mg/L, which reveals that the carbon barrier becomes almost saturated. Continuous filtration after 24 hours is therefore not suggested.

5.2.2.2 UV

From Figure 4-3, the result of UV_{254} has a similar trend as that of TOC, because of the blocking problem in the column. The UV_{254} of the column outflow sample decreases from 0.271 A to 0.04 A within three hours filtration, and then it increases to 0.164 A at the end of twenty-four hour. The TOC of the 24th hour sample is about 92% of the original water sample, which indicates the carbon barrier is 92% saturated. However, the UV_{254} of the same sample is only 61% of the original water sample, which implies the carbon barrier is only 61% saturated. The big difference in the saturation degree from both results could possibly because some natural organic matters in the source water do not have UV-absorbing chemical structures. It also proves that the CBPP AC is more effective in adsorbing light sensitive organic matters. This phenomenon is also observed in the batch test, which may hint that the TOC results are more reliable than the UV results in this study.

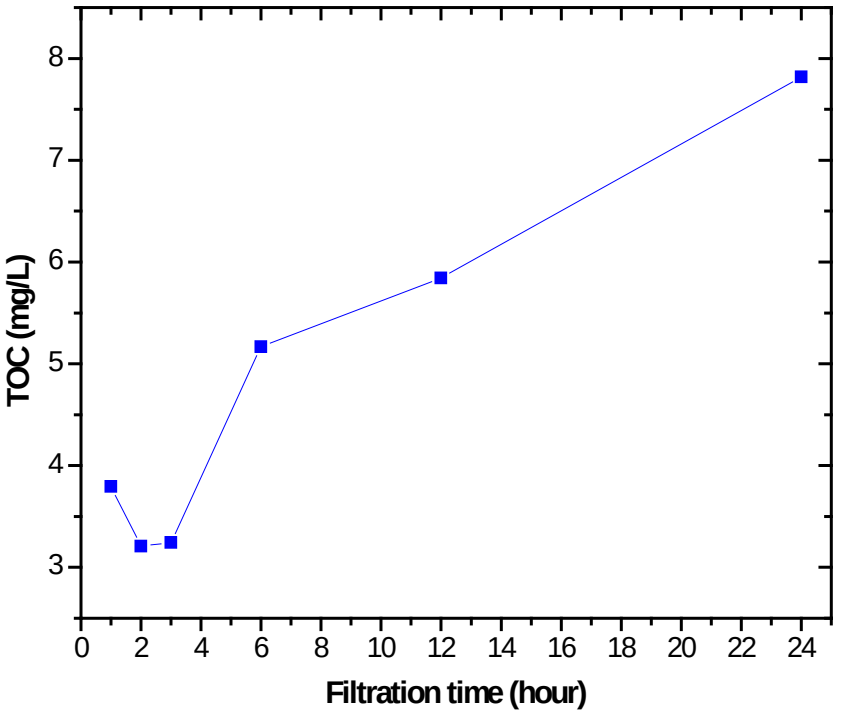

Figure 5-2 TOC concentration in column effluent within 24-hrs filtration

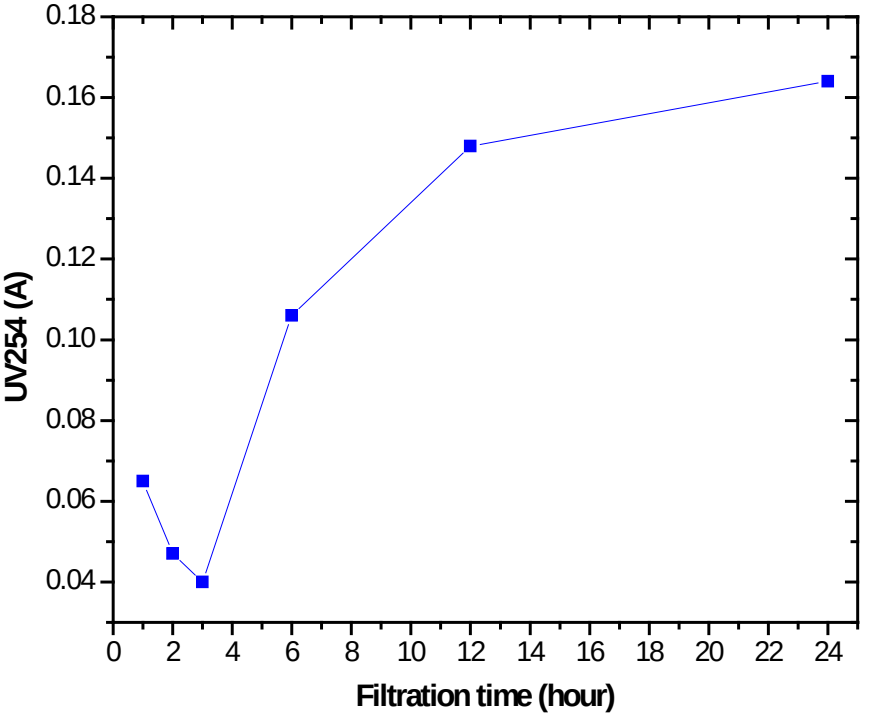

Figure 5-3 UV_{254} in column effluent within 24-hrs filtration

6 Conclusions and Recommendations

6.1 Conclusions

The fly ash generated from Corner Brook Pulp and Paper Ltd. was transformed to activated carbon in a high temperature tube furnace in this study. Effects of two factors including activation temperature and activation time were investigated. Iodine number, methylene blue value, surface microstructure, surface area and pore volume were all analyzed to assess the adsorption capacity of different carbon samples. Iodine number and methylene blue value of a activated carbon sample can have sort of correlations to its surface area and pore volume, the higher the iodine number and methylene blue value are, the larger the surface area and pore volume the sample has. Due to the difficulties in sending multiple samples for analysis in another university, only the clean carbon and the activated carbon with highest iodine number and methylene blue value are sent for BET analysis. In this study, the sample activated under 850 °C for 2 hrs has the highest iodine number (704.53 mg/g) and methylene blue value (193.47 mg/g). Hence, it is selected to conduct further assessment on surface area and pore volume. Comparing the CBPP FA-Clean sample with the CBPP FA-850 °C-2hr sample, it is investigated that the surface area was significantly increased from 486.44 m^2/g to 847.26 m^2/g. Meanwhile, the pore volume increased from 0.18 cm^3/g to 0.28 cm^3/g. The result of scanning electron microscopy also reveals that there are lots of pores developed on the sample surface after activation at 850 °C for 2 hrs.

The generation of activated carbon from fly ash can help CBPP with their waste management, and the activated carbon with high adsorption capacity can have some further applications such as water treatment. Batch test was firstly conducted to evaluate the adsorption efficiency of the CBPP FA-850 °C-2hr on natural organic matter removal. It is revealed that the use of 0.5 g (AC) /L (water) has the highest adsorption effectiveness, and the CBPP AC is more effective in the adsorption of light-sensitive organic matters. A column filtration technology was then developed to further evaluate the adsorption capacity of the activated carbon. The column is 30 cm length and 40 mm diameter, and the CBPP FA-850 °C-2hr sample was placed at the bottom of the column to act as a carbon barrier. Water sample from a local community was continuously passed through the column for 24 hours. The organic matter, measured as total organic matter, in the water sample before and after the filtration was analyzed. Results indicate that more than 60% of the organic matter can be removed by the carbon barrier within 2 hours filtration.

Results also illustrate that the carbon barrier is effective in the decrease of UV_{254}. Above all, the activated carbon generated from CBPP fly ash is proved to be potentially applied in the water treatment area.

6.2 Recommendations

The column filtration experiment was conducted for 24 hours in the laboratory. After 2 hours, the organic matter in the column outflow starts to increase which implies that the activated carbon is gradually getting saturated. Therefore, continuous filtration beyond 24 hours is not suitable for the water sample in this study. To make the activated carbon more applicable in water treatment, the adsorption capacity of the carbon should be further improved, which means the carbon surface area and pore volume should be further developed. Some methods such as chemical, and steam activation are recommended.

Moreover, granular activated carbon is suggested to be applied in a column filtration system, since the use of activated carbon powder can cause blocking problems and difficulties in the flow rate control. More research should be conducted on the granulation of the lab-generated activated carbon and the assessment of its performance in column filtration systems in the future study.

In addition, the regeneration of activated carbon is another point that should be considered in the feasibility study since the regeneration of activated carbon is more convenient and cost-effective to the small communities. The carbon barrier after filtration experiment can be reactivated following the same activation conditions so that the regeneration effect can be evaluated.

Finally, a leaching test should be conducted on the generated activated carbon to make sure no impurities will be leached into the water after treatment.

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Appendix A

BET surface area and porosity analysis report of the CBPP FA-Clean sample.

CCRI University of Ottawa

3Flex 3.01 | 3Flex Version 3.01 Serial # 541 Unit 1 Port 2 | Page 1

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm^3 Measured
Cold free space:	59.7874 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

Summary Report

Surface Area

Single point surface area at p/p° = 0.300000000:	429.8371 m^2/g
BET Surface Area:	486.4352 m^2/g
t-Plot Micropore Area:	402.4971 m^2/g
t-Plot external surface area:	83.9381 m^2/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	68.331 m^2/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	30.8406 m^2/g

Pore Volume

t-Plot micropore volume:	0.181080 cm^3/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.060152 cm^3/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.034851 cm^3/g

Pore Size

BJH Adsorption average pore width (4V/A):	3.5212 nm
BJH Desorption average pore width (4V/A):	4.5201 nm

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
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Cold free space:	59.7874 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm^3/g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
			01:04	755.715210
0.002872266	2.189735	112.1333	09:42	762.371948
0.006061635	4.634561	117.6243	10:56	764.572815
0.024502589	18.696449	126.8301	11:24	763.039734
0.034419968	26.248293	129.0882	11:32	762.589111
0.044503543	33.930656	130.8206	11:38	762.425964
0.063430268	48.394859	133.1425	11:44	762.961609
0.074003917	56.381454	134.1942	11:48	761.871216
0.107937202	82.356895	136.6731	11:52	763.007507
0.142516749	108.754128	138.5169	11:55	763.097168
0.176791744	134.831879	139.9439	11:59	762.659363
0.200549261	153.008804	140.8386	12:02	762.948730
0.243449753	185.739487	142.0199	12:05	762.947937
0.277439118	211.694412	142.8197	12:08	763.030151
0.311649989	237.604889	143.4657	12:11	762.409424
0.344771410	262.964966	144.0148	12:14	762.722656
0.378955097	288.784485	144.4605	12:17	762.054626
0.411615873	314.226990	144.8711	12:20	763.398621
0.446524428	340.769897	145.1849	12:23	763.160706
0.480018489	366.608643	145.4062	12:26	763.738586
0.513930242	392.765259	145.5823	12:29	764.238464
0.547702577	418.930695	145.7175	12:32	764.887207
0.581988349	445.125427	145.8599	12:35	764.835632
0.616795812	471.225525	145.9906	12:39	763.989502
0.649293574	496.677246	146.1514	12:42	764.950195
0.684135730	523.300781	146.3727	12:45	764.907837
0.718272287	548.975281	146.6805	12:48	764.299683
0.734461496	561.574890	146.8563	12:51	764.607666
0.752439678	574.725220	147.0268	12:54	763.815674
0.769448883	587.383301	147.2278	12:57	763.381836
0.777190535	593.345459	147.3222	13:00	763.449158
0.785846377	599.941956	147.4159	13:03	763.434143
0.819256616	625.429321	148.0140	13:06	763.410767
0.852780025	651.611694	148.7798	13:09	764.102905
0.885856969	677.880310	149.7751	13:12	765.225464
0.921911970	704.842102	151.1068	13:15	764.543823
0.955095729	730.103821	152.8303	13:18	764.429993
0.987991802	754.754761	157.6879	13:22	763.928162

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

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Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
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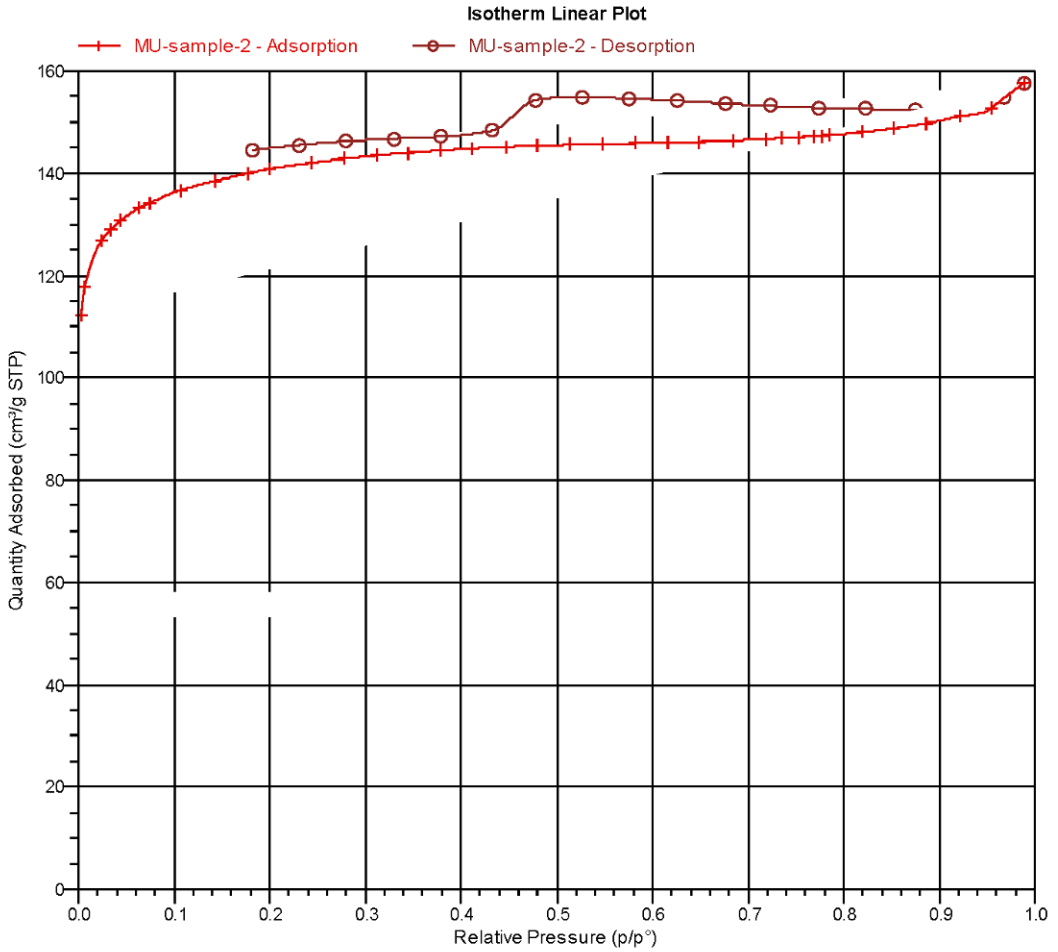
Cold free space:	59.7874 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		



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Operator:
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Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
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Cold free space:	59.7874 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

BET Report

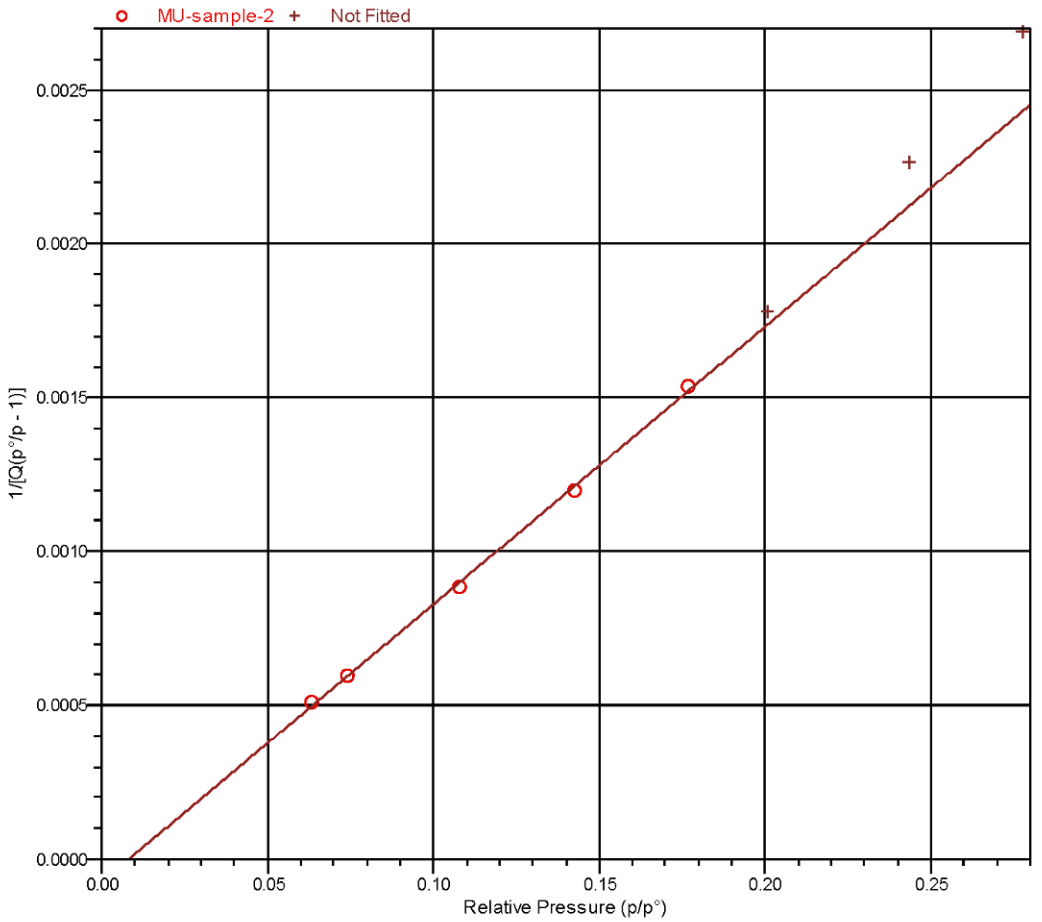
BET surface area: 486.4352 ± 8.5146 m^2/g
Slope: 0.009022 ± 0.000155 g/cm^3 STP
Y-intercept: -0.000074 ± 0.000019 g/cm^3 STP
C: -120.740637
Qm: 111.7579 cm^3/g STP
Correlation coefficient: 0.9995547
Molecular cross-sectional area: 0.1620 nm^2

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)	$1/[Q(p^\circ/p - 1)]$
0.063430268	133.1425	0.000509
0.074003917	134.1942	0.000596
0.107937202	136.6731	0.000885
0.142516749	138.5169	0.001200
0.176791744	139.9439	0.001535

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm³ Measured
Cold free space:	59.7874 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

BET Surface Area Plot



Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm^3 Measured
Cold free space:	59.7874 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

t-Plot Report

Micropore volume:	0.181080 cm^3/g
Micropore area:	402.4971 m^2/g
External surface area:	83.9381 m^2/g
Slope:	54.152554 ± 3.752418 $cm^3/g \cdot nm$ STP
Y-intercept:	116.823166 ± 1.621664 cm^3/g STP
Correlation coefficient:	0.990533
Surface area correction factor:	1.000
Density conversion factor:	0.0015500
Total surface area (BET):	486.4352 m^2/g
Thickness range:	0.35000 nm to 0.50000 nm
Thickness equation:	Harkins and Jura

Thickness Curve

$t = [13.99 / (0.034 - \log(p/p^\circ))]^{0.5}$

t-Plot Report - Data

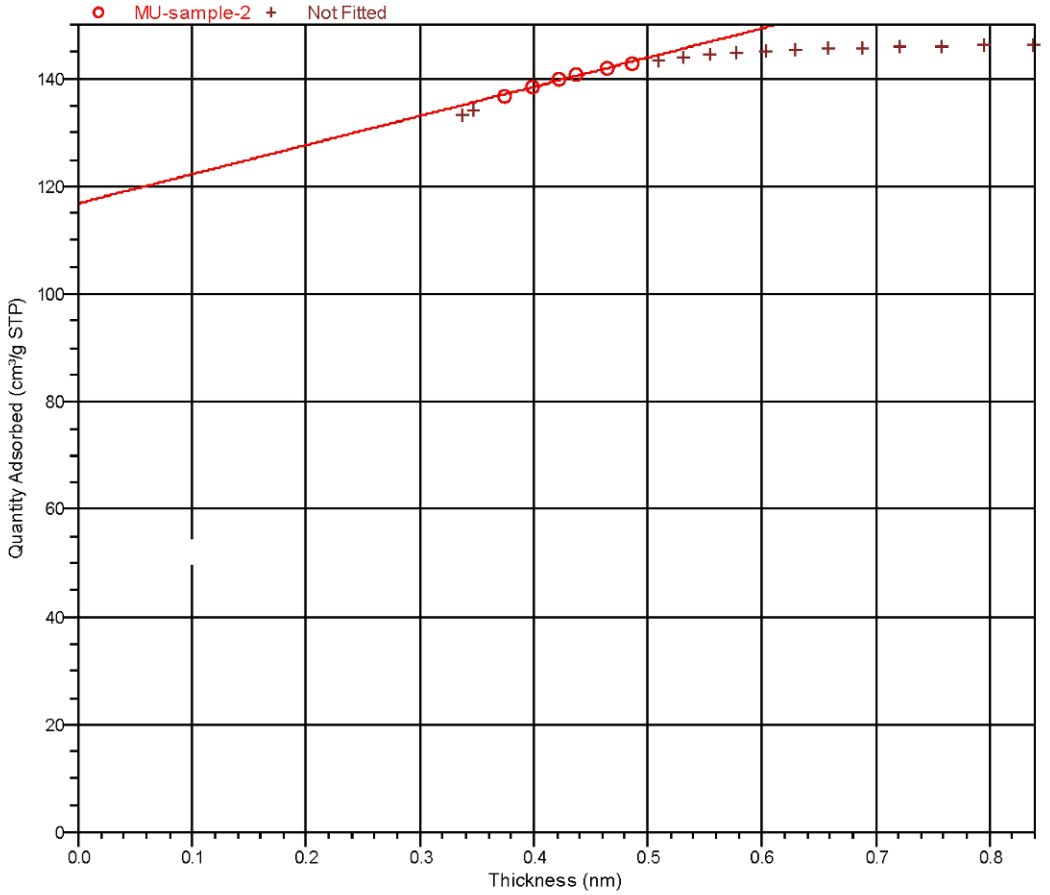
Relative Pressure (p/p°)	Statistical Thickness (nm)	Quantity Adsorbed (cm^3/g STP)	Fitted
0.063430268	0.33702	133.1425	
0.074003917	0.34657	134.1942	
0.107937202	0.37388	136.6731	*
0.142516749	0.39869	138.5169	*
0.176791744	0.42174	139.9439	*
0.200549261	0.43724	140.8386	*
0.243449753	0.46479	142.0199	*
0.277439118	0.48661	142.8197	*
0.311649989	0.50884	143.4657	
0.344771410	0.53084	144.0148	
0.378955097	0.55425	144.4605	
0.411615873	0.57748	144.8711	
0.446524428	0.60347	145.1849	
0.480018489	0.62977	145.4062	
0.513930242	0.65803	145.5823	
0.547702577	0.68812	145.7175	
0.581988349	0.72105	145.8599	
0.616795812	0.75743	145.9906	
0.649293574	0.79463	146.1514	
0.684135730	0.83876	146.3727	

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm³ Measured
Cold free space:	59.7874 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

t-Plot

Harkins and Jura



Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started: 31/08/2016 10:12:37 AM
Completed: 01/09/2016 12:42:16 AM
Report time: 01/09/2016 9:59:02 AM
Sample mass: 0.0797 g
Cold free space: 59.7874 cm³
Low pressure dose: None
Automatic degas: No

Analysis adsorptive: N2
Analysis bath temp.: 77.397 K
Thermal correction: No
Warm free space: 16.6669 cm³ Measured
Equilibration interval: 10 s
Sample density: 1.000 g/cm³

BJH Adsorption Pore Distribution Report

Faas Correction
Kruk-Jaroniec-Sayari
$t = [60.65 / (0.03071 - \log(p/p^\circ))] ^ {0.3968}$

Width range: 1.7000 nm to 300.0000 nm
Adsorbate property factor: 0.95300 nm
Density conversion factor: 0.0015500
Fraction of pores open at both ends: 0.00

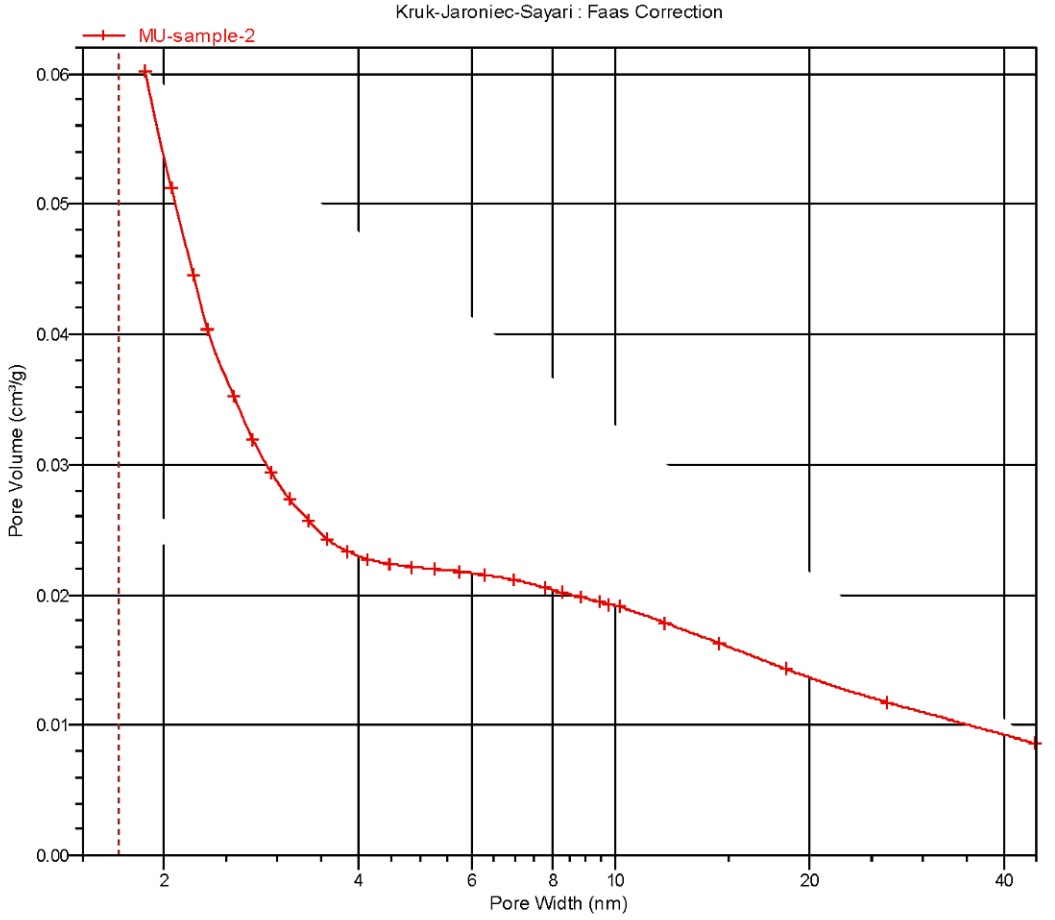
Pore Width Range (nm)	Average Width (nm)	Incremental Pore Volume (cm³/g)	Cumulative Pore Volume (cm³/g)	Incremental Pore Area (m²/g)	Cumulative Pore Area (m²/g)
161.6 - 44.8	52.4	0.008586	0.008586	0.655	0.655
44.8 - 26.4	30.9	0.003151	0.011736	0.408	1.063
26.4 - 18.5	21.0	0.002557	0.014293	0.488	1.551
18.5 - 14.5	16.0	0.001992	0.016286	0.499	2.050
14.5 - 11.9	13.0	0.001565	0.017851	0.483	2.534
11.9 - 10.2	10.9	0.001237	0.019088	0.454	2.988
10.2 - 9.8	10.0	0.000173	0.019261	0.069	3.057
9.8 - 9.5	9.6	0.000185	0.019446	0.077	3.134
9.5 - 8.8	9.1	0.000400	0.019846	0.175	3.310
8.8 - 8.3	8.5	0.000323	0.020169	0.151	3.461
8.3 - 7.8	8.0	0.000363	0.020532	0.181	3.642
7.8 - 7.0	7.3	0.000619	0.021150	0.338	3.980
7.0 - 6.3	6.6	0.000389	0.021540	0.237	4.216
6.3 - 5.7	6.0	0.000247	0.021786	0.165	4.381
5.7 - 5.2	5.5	0.000152	0.021938	0.111	4.492
5.2 - 4.8	5.0	0.000218	0.022156	0.174	4.666
4.8 - 4.5	4.6	0.000215	0.022371	0.186	4.852
4.5 - 4.1	4.3	0.000386	0.022757	0.360	5.212
4.1 - 3.9	4.0	0.000584	0.023341	0.586	5.798
3.9 - 3.6	3.7	0.000969	0.024310	1.044	6.842
3.6 - 3.4	3.5	0.001427	0.025737	1.647	8.488
3.4 - 3.1	3.2	0.001575	0.027312	1.944	10.432
3.1 - 2.9	3.0	0.002089	0.029401	2.757	13.189
2.9 - 2.7	2.8	0.002545	0.031945	3.592	16.780
2.7 - 2.6	2.6	0.003338	0.035284	5.047	21.827
2.6 - 2.3	2.4	0.005096	0.040380	8.357	30.184
2.3 - 2.2	2.3	0.004164	0.044544	7.309	37.493
2.2 - 2.1	2.1	0.006660	0.051204	12.516	50.009
2.1 - 1.9	2.0	0.008948	0.060152	18.322	68.331

Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm³ Measured
Cold free space:	59.7874 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

BJH Adsorption Cumulative Pore Volume (Larger)

Kruk-Jaroniec-Sayari : Faas Correction

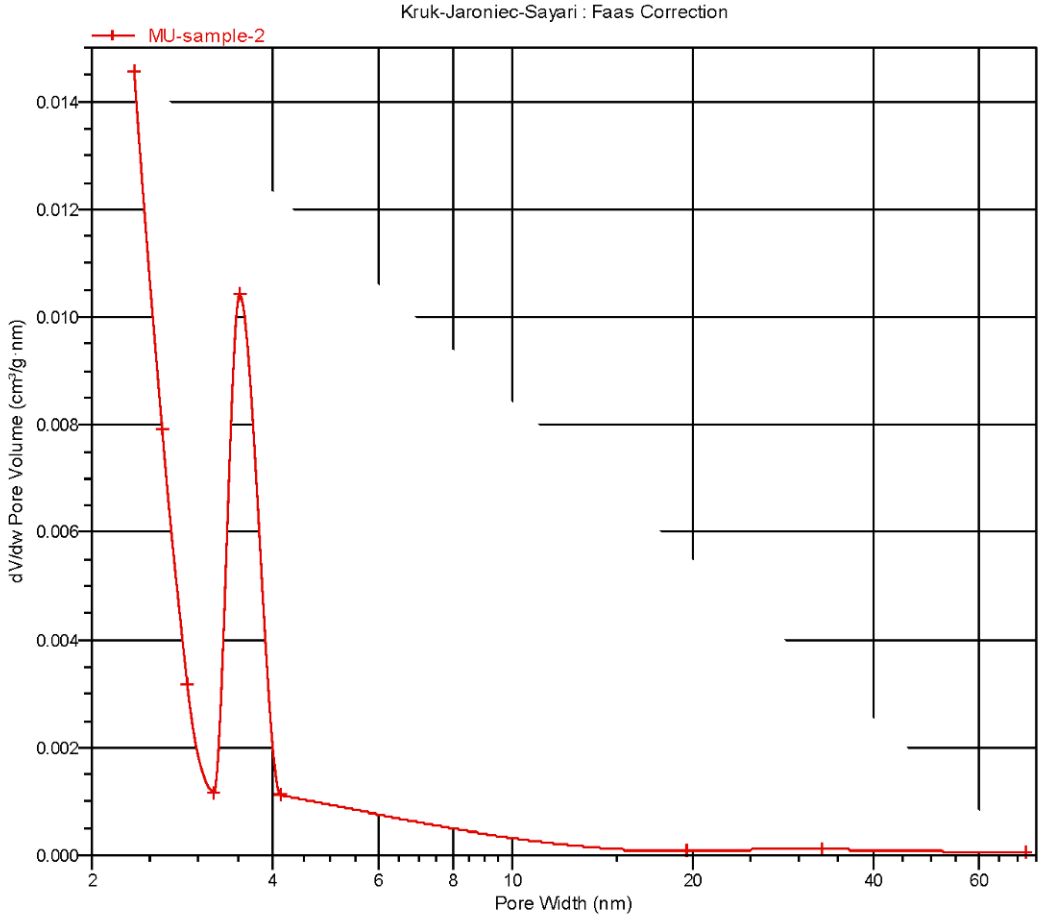


Sample: MU-sample-2
Operator:
File: C:\3Flex\data\Yong Yang data\000-326-MU-sample-2.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.397 K
Report time:	01/09/2016 9:59:02 AM	Thermal correction:	No
Sample mass:	0.0797 g	Warm free space:	16.6669 cm³ Measured
Cold free space:	59.7874 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

BJH Desorption dV/dw Pore Volume

Kruk-Jaroniec-Sayari : Faas Correction



Appendix B

BET surface area and porosity analysis report of the CBPP AC-850°C-2hr sample.

CCRI University of Ottawa

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Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm³ Measured
Cold free space:	61.5803 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

Summary Report

Surface Area

Single point surface area at p/p° = 0.300000000:	756.1617 m²/g
BET Surface Area:	847.2587 m²/g
t-Plot Micropore Area:	619.4937 m²/g
t-Plot external surface area:	227.7650 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	197.099 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	142.9051 m²/g

Pore Volume

t-Plot micropore volume:	0.278697 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.215505 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.186968 cm³/g

Pore Size

BJH Adsorption average pore width (4V/A):	4.3735 nm
BJH Desorption average pore width (4V/A):	5.2333 nm

Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started: 31/08/2016 10:12:37 AM
Completed: 01/09/2016 12:42:16 AM
Report time: 01/09/2016 9:57:09 AM
Sample mass: 0.0783 g
Cold free space: 61.5803 cm³
Low pressure dose: None
Automatic degas: No

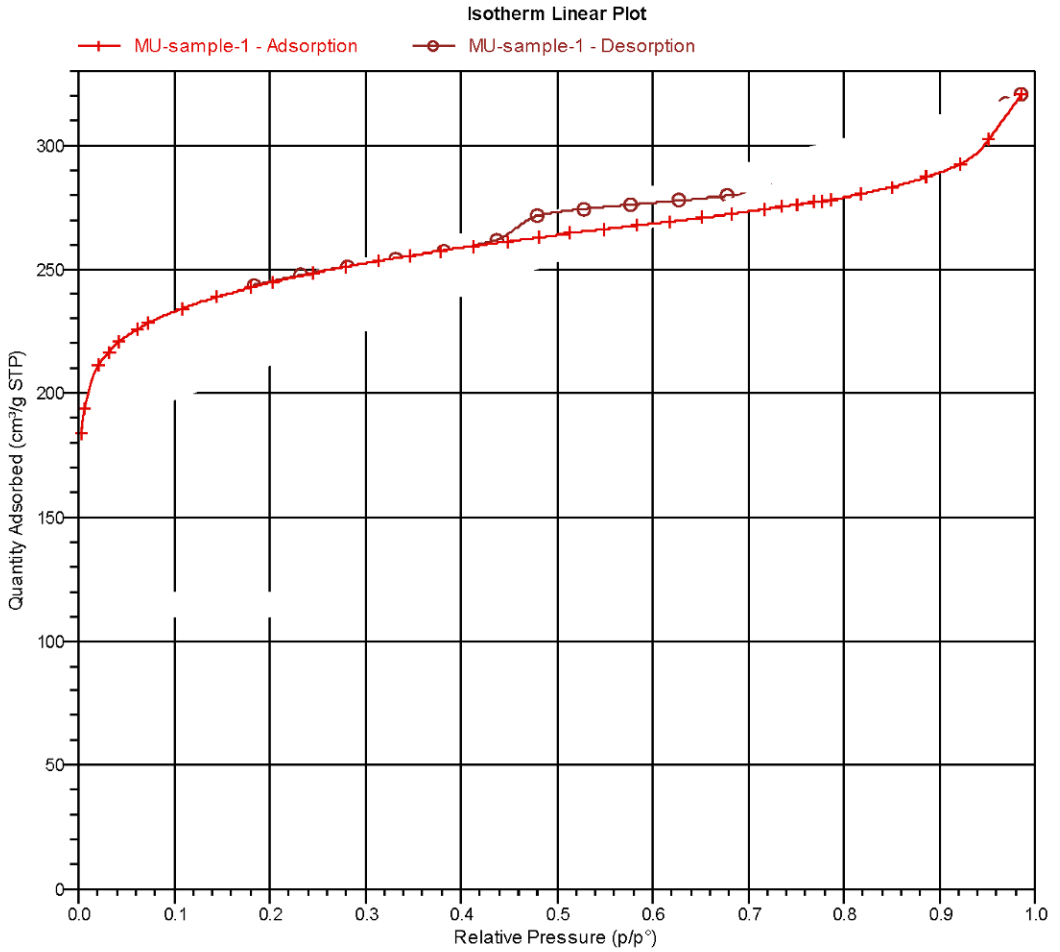
Analysis adsorptive: N2
Analysis bath temp.: 77.377 K
Thermal correction: No
Warm free space: 17.1518 cm³ Measured
Equilibration interval: 10 s
Sample density: 1.000 g/cm³

Isotherm Tabular Report

Relative Pressure (p/p°)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm³/g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
			01:04	755.715210
0.002853270	2.173656	183.9589	04:23	761.812317
0.005805263	4.430001	193.6831	04:36	763.100830
0.021836203	16.652920	211.4856	04:47	762.628906
0.032162341	24.539495	216.7341	04:53	762.988464
0.042912548	32.746700	220.7136	04:58	763.103149
0.061327646	46.729656	225.6686	05:04	761.967224
0.073981690	56.453331	228.3956	05:08	763.071655
0.108227429	82.679375	234.1632	05:13	763.941040
0.144680470	110.314575	238.8225	05:17	762.470398
0.179704454	136.866440	242.5605	05:21	761.619629
0.203758315	155.271484	244.8577	05:25	762.037537
0.245446167	187.027298	248.3693	05:28	761.989075
0.279612647	213.078644	250.9664	05:31	762.049377
0.314283085	239.513367	253.3514	05:36	762.094360
0.347047902	264.267975	255.4514	05:39	761.474060
0.379510806	289.409882	257.4207	05:42	762.586670
0.413647464	315.649017	259.3439	05:47	763.087036
0.448185672	341.710938	261.1817	05:50	762.431641
0.480748189	367.049805	262.8412	05:53	763.497009
0.514210600	392.793030	264.4838	05:58	763.875793
0.549634456	419.566803	266.1120	06:01	763.356079
0.583566191	445.140045	267.6359	06:04	762.792725
0.618156015	470.834503	269.2112	06:07	761.675842
0.652735752	496.200165	270.7693	06:12	760.185364
0.683128134	519.772034	272.3278	06:15	760.870483
0.716843830	546.045593	274.1682	06:18	761.735779
0.734856680	559.664856	275.1790	06:21	761.597290
0.751895907	573.061890	276.1241	06:26	762.155884
0.768466627	585.702759	277.0729	06:29	762.170715
0.777371381	592.391296	277.5921	06:32	762.044128
0.786724682	598.810181	278.0577	06:35	761.143250
0.818280308	622.763855	280.3083	06:38	761.064209
0.850679066	649.224670	283.2351	06:42	763.184021
0.886639268	676.587585	287.1024	06:46	763.092285
0.921384981	702.105591	292.5147	06:50	762.011108
0.951571227	725.475952	302.0846	06:54	762.397949
0.984673751	749.979431	320.3032	07:00	761.652710

Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm³ Measured
Cold free space:	61.5803 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		



Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm^3 Measured
Cold free space:	61.5803 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

BET Report

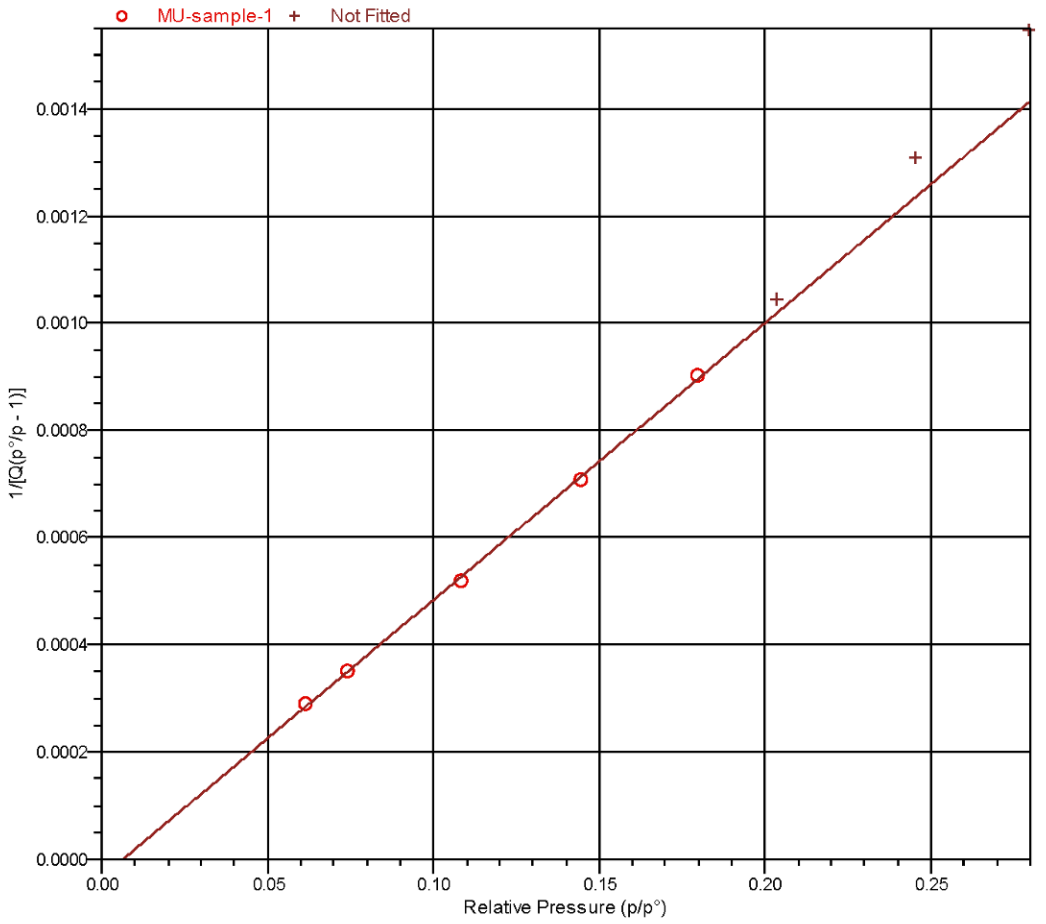
BET surface area: 847.2587 ± 13.5370 m^2/g
Slope: 0.005171 ± 0.000081 g/cm^3 STP
Y-intercept: -0.000034 ± 0.000010 g/cm^3 STP
C: -153.312025
Qm: 194.6567 cm^3/g STP
Correlation coefficient: 0.9996278
Molecular cross-sectional area: 0.1620 nm^2

Relative Pressure (p/p°)	Quantity Adsorbed (cm^3/g STP)	$1/[Q(p^\circ/p - 1)]$
0.061327646	225.6686	0.000290
0.073981690	228.3956	0.000350
0.108227429	234.1632	0.000518
0.144680470	238.8225	0.000708
0.179704454	242.5605	0.000903

Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm³ Measured
Cold free space:	61.5803 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

BET Surface Area Plot



Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm^3 Measured
Cold free space:	61.5803 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

t-Plot Report

Micropore volume:	0.278697 cm^3/g
Micropore area:	619.4937 m^2/g
External surface area:	227.7650 m^2/g
Slope:	146.958047 ± 5.903053 $cm^3/g \cdot nm$ STP
Y-intercept:	179.820610 ± 2.559442 cm^3/g STP
Correlation coefficient:	0.996789
Surface area correction factor:	1.000
Density conversion factor:	0.0015499
Total surface area (BET):	847.2587 m^2/g
Thickness range:	0.35000 nm to 0.50000 nm
Thickness equation:	Harkins and Jura

Thickness Curve

$t = [13.99 / (0.034 - \log(p/p^\circ))]^{0.5}$

t-Plot Report - Data

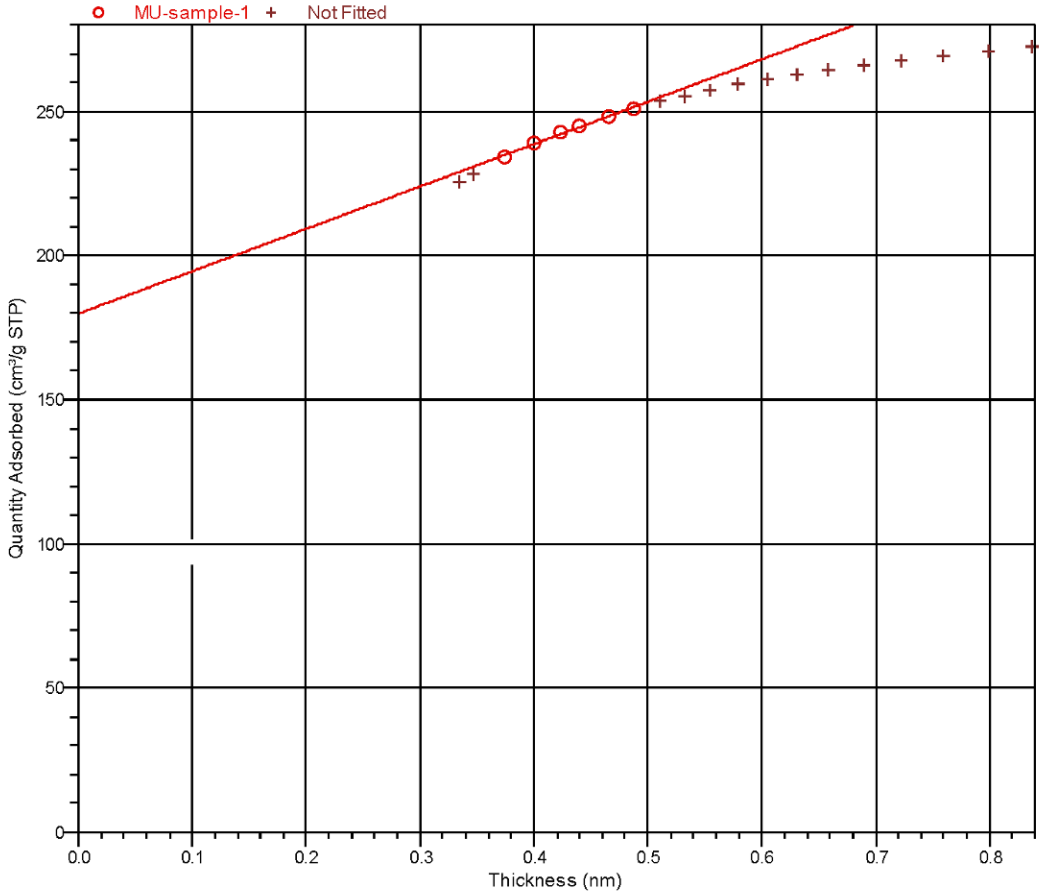
Relative Pressure (p/p°)	Statistical Thickness (nm)	Quantity Adsorbed (cm^3/g STP)	Fitted
0.061327646	0.33503	225.6686	
0.073981690	0.34655	228.3956	
0.108227429	0.37410	234.1632	*
0.144680470	0.40018	238.8225	*
0.179704454	0.42366	242.5605	*
0.203758315	0.43931	244.8577	*
0.245446167	0.46607	248.3693	*
0.279612647	0.48801	250.9664	*
0.314283085	0.51057	253.3514	
0.347047902	0.53237	255.4514	
0.379510806	0.55464	257.4207	
0.413647464	0.57896	259.3439	
0.448185672	0.60474	261.1817	
0.480748189	0.63036	262.8412	
0.514210600	0.65827	264.4838	
0.549634456	0.68991	266.1120	
0.583566191	0.72263	267.6359	
0.618156015	0.75892	269.2112	
0.652735752	0.79878	270.7693	
0.683128134	0.83741	272.3278	

Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm³ Measured
Cold free space:	61.5803 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

t-Plot

Harkins and Jura



Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm^3 Measured
Cold free space:	61.5803 cm^3	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm^3
Automatic degas:	No		

BJH Adsorption Pore Distribution Report

Faas Correction
Kruk-Jaroniec-Sayari
$t = [60.65 / (0.03071 - \log(p/p^\circ))] ^ {0.3968}$

Width range: 1.7000 nm to 300.0000 nm
Adsorbate property factor: 0.95300 nm
Density conversion factor: 0.0015499
Fraction of pores open at both ends: 0.00

Pore Width Range (nm)	Average Width (nm)	Incremental Pore Volume (cm^3/g)	Cumulative Pore Volume (cm^3/g)	Incremental Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
127.2 - 41.7	49.3	0.032419	0.032419	2.631	2.631
41.7 - 26.3	30.4	0.017796	0.050216	2.339	4.970
26.3 - 18.6	21.0	0.010312	0.060528	1.962	6.932
18.6 - 14.3	15.8	0.007571	0.068099	1.911	8.843
14.3 - 11.9	12.8	0.005928	0.074027	1.846	10.689
11.9 - 10.2	10.9	0.004602	0.078629	1.689	12.378
10.2 - 9.8	10.0	0.000890	0.079519	0.357	12.734
9.8 - 9.4	9.6	0.001061	0.080580	0.442	13.176
9.4 - 8.8	9.1	0.001974	0.082554	0.867	14.044
8.8 - 8.3	8.5	0.002003	0.084557	0.940	14.983
8.3 - 7.8	8.0	0.002208	0.086766	1.105	16.088
7.8 - 6.9	7.3	0.004147	0.090912	2.272	18.360
6.9 - 6.3	6.6	0.003590	0.094502	2.172	20.532
6.3 - 5.8	6.0	0.003573	0.098075	2.375	22.907
5.8 - 5.3	5.5	0.003782	0.101857	2.758	25.665
5.3 - 4.8	5.0	0.003774	0.105631	2.997	28.662
4.8 - 4.5	4.6	0.004209	0.109840	3.628	32.290
4.5 - 4.2	4.3	0.004486	0.114326	4.177	36.467
4.2 - 3.9	4.0	0.004704	0.119030	4.704	41.172
3.9 - 3.6	3.7	0.005405	0.124435	5.801	46.973
3.6 - 3.4	3.5	0.005882	0.130317	6.771	53.743
3.4 - 3.2	3.3	0.006281	0.136598	7.729	61.472
3.2 - 3.0	3.0	0.006896	0.143493	9.055	70.527
3.0 - 2.8	2.8	0.008091	0.151585	11.367	81.894
2.8 - 2.6	2.7	0.009180	0.160764	13.819	95.713
2.6 - 2.4	2.5	0.012844	0.173608	20.940	116.653
2.4 - 2.2	2.3	0.008701	0.182309	15.172	131.826
2.2 - 2.1	2.1	0.014504	0.196813	27.099	158.925
2.1 - 1.9	2.0	0.018692	0.215505	38.175	197.099

Sample: MU-sample-1
Operator:
File: C:\3Flex\data\Yong Yang data\000-325-MU-sample-1.SMP

Started:	31/08/2016 10:12:37 AM	Analysis adsorptive:	N2
Completed:	01/09/2016 12:42:16 AM	Analysis bath temp.:	77.377 K
Report time:	01/09/2016 9:57:09 AM	Thermal correction:	No
Sample mass:	0.0783 g	Warm free space:	17.1518 cm³ Measured
Cold free space:	61.5803 cm³	Equilibration interval:	10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

BJH Desorption dV/dw Pore Volume

Kruk-Jaroniec-Sayari : Faas Correction